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Comparative Cadmium Adsorption from Water by Nanochitosan and Chitosan

Seyed Masoud Seyedi, Bagher Anvaripour, Mohsen Motavassel, Naghi Jadidi

Abstract*—Chitosan and nanochitosan were used for the adsorption of cadmium from water. Nanochitosan was prepared from chitosan by using sodium tripolyphosphate. Cadmium removal was a pH dependent and the optimum adsorptions of chitosan and nanochitosan were found at pH solutions of 7.0 and 4.6 respectively. The maximum adsorption capacities for chitosan and nanochitosan adsorbents were 153 and 358 mg/g respectively. Experimental data were correlated better by the model of Langmuir than with Freundlich model. Kinetics of the adsorption described better with the pseudo-second order model for both adsorbents and the maximum adsorption capacities for both adsorbents were at a temperature of 28°C.

***Index Terms*—Cadmium, Adsorption, Nanochitosan particle, Adsorption isotherm, Adsorption kinetics.**

I. INTRODUCTION

Pollution by heavy metals is a serious environmental problem [1]. These metals are toxic, not biodegradable and tend to accumulate in tissues of living organisms that causes variant disorders [2]–[7]. Industrial activities are the main sources of heavy metals such as metal plating, oil refining, petrochemical, dyeing and paints, mining operations, fertilizers and pesticides [2], [8]. Cadmium (Cd) is a heavy metal with atomic number 48. The major industrial sources of Cd are metallurgy, battery production and electroplating [9], [10]. Cd toxicity is such that low concentrations of Cd in water cause diseases such as nephritis, hypertension, renal dysfunction, nervous system dysfunction and digestive system dysfunction [6], [11]–[13]. Therefore Cd removal from water is very important. Chemical precipitation, adsorption, ion exchange, evaporation, solvent extraction, reverse osmosis, advanced oxidation and membrane processes are commonly methods that have been used to remove heavy metals. Each of these methods has advantages and disadvantages [3], [5], [6], [8], [11], [14]–[16]. Adsorption is widely used for removal of heavy metals because it is more effective, economical, high efficient [17]. In recent years low-cost adsorbents that are produced from wastes have been used widely [17]. Chitosan (CTS) is one of the low-cost absorbent [18]. Chitosan is obtained by deacetylation of chitin that is a type of natural polymer [5], [17]–[20]. Although CTS exists in fungal biomass and insect cuticle but the main sources of CTS are crabs and shrimp shells and other crustaceans [9], [19]–[21]. Amino groups in the structure of this polysaccharide absorbent cause increasing uptake ability and adsorption capacity [4], [9], [14], [16], [17], [19], [22]. Recently CTS has been very popular among researchers because it has good properties such as abundance, non-toxicity, biodegradability and adsorption properties [8]. Reforming chitosan became more resistant to lower pH compared to common chitosan [14]. Literature showed that pH is an important factor that could make a major change in the adsorption capacity [18], [23]. Cadmium removal from water by chitosan has been investigated by some researchers. The adsorption capacity of 150 mg/g was reported for CTS in the cadmium removal from water [9]. The chemical properties of CTS were improved by cross linking, but it reduced its adsorption capacity to 83.75 mg/g [8]. CTS cross linked with Schiff's based had an adsorption capacity of 84 mg/g in cadmium removal from water [14]. Polyaspartic acid was useful in the removal of adsorbed ions from CTS [18]. Although the adsorption capability of chitosan in removing cadmium from water has been studies, however there is a lack of sufficient data about the removal capacity of cadmium by nanochitosan. The purposes of this research is to compare the removal of Cd by the CTS and nano CTS and to investigate the effect of some parameters such as temperature, initial concentration, solution pH on Cd uptake. The kinetics also is investigated.

II. MATERIAL AND METHODS

A. Material

Sodium tripolyphosphate (STPP), NaCl, Acetic acid (CH_3COOH), HCl and NaOH, were obtained from Merck (Germany). Cadmium chloride dihydrate was purchased from Fluka (Switzerland). Chitosan (CTS) with a degree of deacetylation more than 90% and a viscosity of less than 200 mPa.s was purchased from Zhejiang Aoxing Biotechnology Co. Ltd (China).

B. Preparation of chitosan nanodispersion

Two grams of CTS was dissolved in one liter of 0.5% (volume percent) aqueous acetic acid, and then 3 g of NaCl was added to the new solution gently. After that STPP (2 g/L) was added into the chitosan solution drop-wise under magnetic stirring at room temperature. After 5 min stirring with a speed of 1000 rpm, a milky dispersion with a pH of 4.6 was obtained [7], [17].Particle size of the prepared nanochitosan was investigated by using a dynamic light scattering (DLS) device (zeta plus from Brookhaven) and the average particle size of nanochitosan was 34.6 nm.

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III. ADSORPTION EXPERIMENTS

A. *Effect of pH*

Uptake experiments were performed at controlled pH and 28°C by shaking 50 ml of nanochitosan solution with 50 mL (1000 mg/L) of the Cd solution for 12 hours at 300 rpm. HCl and NaOH used for adjusting the pH of the medium; pH was adjusted at 2, 3, 4, 5 and 6. The centrifuge model EBA 8 used for separating solid and liquid phases for 30 min at 6000 rpm. At the end of the experiment the residual concentration of Cd ions in water was determined using a PerkinElmer Analyst 700 atomic absorption spectrophotometer.

B. *Effect of the initial concentration of the metal ions*

Uptake experiments were performed at pH 4.6 and 28°C by shaking 50 ml of nanochitosan solution with 50 mL of the Cd solution in a series Erlenmeyer flask for 12 hr at 300 rpm. The initial concentration of Cd ion was adjusted at 0.5, 1, 10, 50, 100, 500, 800, and 1000 mg/L. HCl and NaOH used for adjusting the pH of the medium. After adsorption, solid and liquid phases were separated and the residual concentration of the Cd ions was measured using PerkinElmer optima 730 DV ICP.

C. *Effect of contact time*

Uptake experiments were performed at pH 4.6 and 28°C by shaking 50 ml of nanochitosan solution with 50 mL (1000 mg/L) of the Cd solution in a series of Erlenmeyer flask for 10, 20, 30, 40, 50 and 60 min at 300 rpm. HCl and NaOH used for adjusting the pH of the medium. After adsorption, solid and liquid phases were separated and the residual concentration of the Cd ions in the aqueous phase was measured using PerkinElmer optima 730 DV ICP.

D. *Effect of the temperature*

Uptake experiments were performed at pH 4.6 by shaking 50 ml of nanochitosan solution with 50 mL (1000 mg/L) of the Cd solution in a series of Erlenmeyer flasks for 12 hours at 300 rpm. HCl and NaOH used for adjusting the pH of the medium. Temperature was adjusted at 15, 30, 45 and 60°C. After adsorption, solid and liquid phases were separated and the residual concentration of the Cd ions was measured using PerkinElmer optima 730 DV ICP.

IV. RESULTS AND DISCUSSION

A. *Effect of pH on Cd removal*

Fig. 1 shows effect of pH on cadmium removal by chitosan and nanochitosan. In this experiments involving chitosan, pH range of the solution was varied from 4 to 10. At low pH, hydronium ions have high concentration and hydronium ions compete with Cd ions for adsorption that decreased the adsorption capacity. However, as pH of solution increased the cadmium uptake increased probably due to the decreased hydronium ions concentration that provided more adsorption sites for cadmium ions. The optimum pH for Cd removal by chitosan appeared at pH 7 which is in accord with the literature [8-9]. The adsorption increased sharply at pH above 8 that may be related to cadmium hydroxide formation.

In the nanochitosan study the pH range was 2–7. As was shown in Fig. 1, increasing the pH increases the adsorption of Cd due to reducing the hydronium ions.

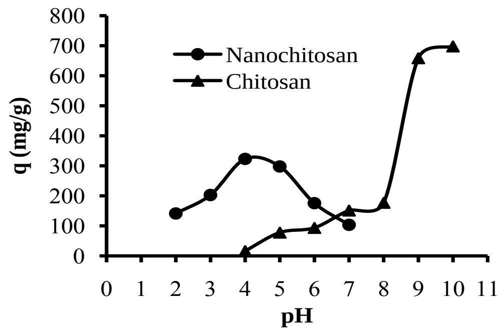

Fig. 1 – Effect of pH on Cd adsorption at 300 rpm and 28°C.

The optimum pH for nanochitosan was around 4.6. Increasing the pH further was resulted in a decreased in adsorption capacity that may be attributed to the increased size of nanochitosan particles that decreased the surface area for cadmium ion uptake. At pH of 7 the adsorption capacities of nanochitosan and chitosan solution were the same.

B. *Adsorption isotherms*

The adsorption isotherms of cadmium by chitosan and nanochitisan are shown in Fig. 2. As shown in this figure, nanochitosan particles have a higher cadmium uptake that can be related to their higher surface areas compared to chitosan particles. The assumption of Langmuir isotherm is based on the monolayer adsorption onto a surface without any interaction between the particles. The linear form of Langmuir model can be illustrated by the following equation [5], [14]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{1}$$

Where C_e is the equilibrium Cd concentration in the solution (mg/L), q_e the amount of metal ion adsorbed on adsorbent chitosan or nanochitosan (mg/g), q_m is amount of metal ion for a formation of a monolayer adsorbate on adsorbent surface (mg/g), K_L is Langmuir equilibrium constant that depends on the absorbed energy (L/mg). The Freundlich isotherm is another popular isotherm that is used widely to express adsorption equilibrium at constant temperature. The linear form of this model is shown by the following [5], [14]:

$$\ln(q_e) = \ln K_F + \frac{1}{n}\ln C_e \tag{2}$$

Where K_F is Freundlich isotherm constant that shows adsorption potential and n is Freundlich equilibrium constant that expresses the binding energy between adsorbent and metal ions. Langmuir and Freundlich equations were used to fit the experimental data. The isotherm constants for these models were found by a linear regression and the results are

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shown in Table 1. For both CTS and nanoCTS, the Langmuir models fitted experimental data better than Freundlich models that reflect the suitability of a monolayer adsorption. The maximum amounts of adsorption capacity predicted by Langmuir models for CTS and nanoCTS were 153.85 and 357.14 mg/g which matched with experimentally data. The data of cadmium adsorbent by chitosan is consistent with the literature that indicates chitosan is very useful for removing Cd with adsorption capacity more than 150 mg/g [9]. Cd adsorption obeys Langmuir model and maximum adsorption of Cd in presence of Ni and Cu ions was 84 mg/g [14]. Cd adsorption is a monolayer process of adsorbate [13].

Table 1: Langmuir and Freundlich isotherms constants.

Adsorbent	Langmuir			Freundlich		
	q_m	10^2K_L	R^2	K_F	n_F	R^2
CTS	153	2.32	0.9998	3.06	1.48	0.9500
NanoCTS	358	4.45	0.9944	15.7	1.78	0.9884

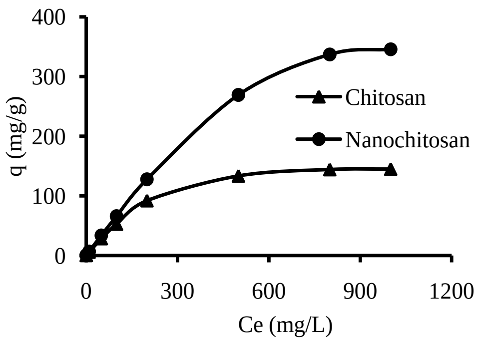

Fig. 2 − Effect of Cd Concentration on Capacity at 28°C.

C. Adsorption Kinetics

A suitable adsorbent for water treatment must not only have a high capacity but also a fast adsorption rate. Adsorption rate is one of the important properties of adsorbent. Kinetic models are used to survey the controlling parameters of adsorption processes, such as adsorption rate, chemical reaction and diffusion mechanisms [17]. Fig. 3 shows the effect of contact time on Cd adsorption by CTS and nanoCTS. Approximate equilibrium times for the nanoCTS and CTS were 50 and 150 minutes respectively as demonstrated in Fig. 3. For kinetics study the models of pseudo-first order and pseudo-second order were used. Equation (2) shows the linear form of pseudo-first order model [5], [14]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (3)$$

Where q_t (mg/g) is amounts of metal ion adsorbed at time t, K_1 is the constant coefficient of pseudo-first-order rate of adsorption (min^{-1}). Linear form of pseudo-second order model is given by the following equation [5], [14]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Where K_2 is the rate constant of pseudo-second order adsorption. The fitted parameters of the two kinetic models are reported in Table 2. The pseudo-second order model fitted the experimental data better than pseudo-first did as shown in Table 2. Literature showed that pseudo-second order model fitted their experimental data better than pseudo-first model did [11], [14], [15], [17].

Table 2: First Order and Pesudo-Second Order Models Constants.

Adsorbent	Pseudo-first order			Pseudo-second order		
	10^2K_1	q_e	R^2	10^4K_2	q_e	R^2
CTS	2.87	68.6	0.9291	5.13	158	0.9994
NanoCST	11.3	213	0.9668	8.75	377	0.9997

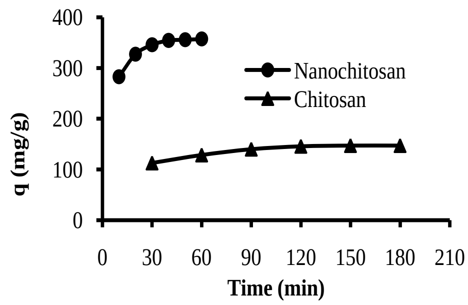

Fig. 3 − Effect of contact time on Cd adsorption at 28°C.

D. Effect of temperature on Cd removal

Fig. 4 shows the effect of temperature on Cd adsorption at 300 rpm stirring and a contact time of 12 hr. The maximum removal was occurred at 28°C for both chitosan and nanochitosan. Increasing Cd adsorption at temperature of 28°C may be related to the reduced energy of binding between water molecules and chitosan surface that enhances Cd adsorption on chitosan surface. At lower temperatures, the energy binding between water molecules and chitosan surface is strong but increasing temperature causing this energy to reduce. The decrease in Cd removal at temperatures above 28°C may be attributed to the increase of Cd ions solubility in water that reduces driving force for adsorption and therefore cause a decrease in adsorption capacity.

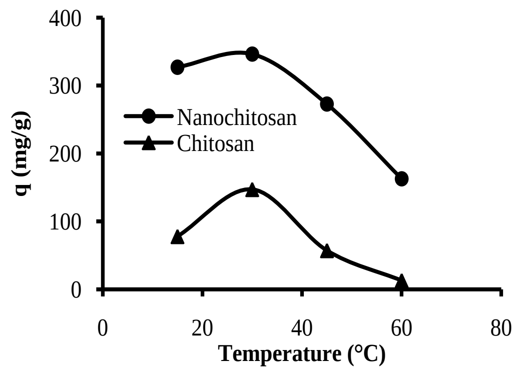

Fig. 4 − Effect of Temperature on Cd Adsorption.

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V. CONCLUSION

The adsorption of cadmium from water by chitosan and nanochitosan has been investigated. Nanochitosan with a mean particle size of 34.6 nm was prepared. The Cd adsorbent was sensitive to pH and maximum uptakes by chitosan and nanochitosan were occurred respectively at pH 7 and 4.6. Langmuir adsorption model fitted well for both adsorbants. The nanochitosan had more adsorption capacity and faster adsorption kinetics than chitosan. The second order model described better the adsorption kinetics than first order did. Cd uptake depended on temperature and the maximum cadmium removal was happened at 28°C for both adsorbents.

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AUTHOR BIOGRAPHY

Seyed Masoud Seyedi Currently is a Master of Science student in Chemical Engineering (Health, Environment, and Safety) at the Petroleum University of Technology, Abadan, Iran.

Bagher Anvaripour Currently is an assistant professor at the Petroleum University of Technology, Abadan, Iran.

Mohsen Motavassel Currently is an instructor at the Petroleum University of Technology, Abadan, Iran.

Naghi Jadidi Currently is an assistant professor at the Petroleum University of Technology, Abadan, Iran.